

AD/A-002 668

KINETICS AND MECHANISM IN THE OXIDATION
OF METAL VAPORS

Peter Zavitsanos, et al

General Electric Company

Prepared for:

Rome Air Development Center
Defense Advanced Research Projects Agency

October 1974

DISTRIBUTED BY:



National Technical Information Service
U. S. DEPARTMENT OF COMMERCE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER RADC-TR-74-292	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER AD/A-002668
4. TITLE (and Subtitle) Kinetics and Mechanism in the Oxidation of Metal Vapors		5. TYPE OF REPORT & PERIOD COVERED Final Technical Report Feb 76 - Jul 74
7. AUTHOR(s) Dr. Peter Zavitsanos Joseph A. Golden		6. PERFORMING ORG. REPORT NUMBER N/A
9. PERFORMING ORGANIZATION NAME AND ADDRESS General Electric/RESD 3198 Chestnut Street Philadelphia PA 19104		8. CONTRACT OR GRANT NUMBER(s) F30602-73-C-0121
11. CONTROLLING OFFICE NAME AND ADDRESS Defense Advanced Research Projects Agency 140 Wilson Blvd Arlington VA 22209		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 62301E 16490303
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) Rome Air Development Center (OCSE) Griffiss AFB NY 13441		12. REPORT DATE October 1974
		13. NUMBER OF PAGES 20
		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE N/A
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) Same		
18. SUPPLEMENTARY NOTES Project Engineer: Joseph J. Simons (OCSE) Griffiss AFB NY 13441 AC 315 330-3055		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Kinetics Uranium Thorium Reproduced by NATIONAL TECHNICAL INFORMATION SERVICE US Department of Commerce Springfield, VA. 22151		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The results of laboratory experiments designed to gain an understanding of the kinetics and mechanism of gas-phase metal oxidation reactions of thorium and uranium are presented. The experiments were conducted in an apparatus which utilizes RF heating and laser radiation for the production of the metal vapor and time-of-flight mass spectrometry for product identification and quantitative measurements of reactants and products. Measurements were made		

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

on the oxidation of thorium and uranium by molecular and atomic oxygen, as well as N₂O, and values of the rate constants are given.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

KINETICS & MECHANISM IN THE OXIDATION OF
METAL VAPORS

Dr. Peter Zavitsanos
Joseph A. Golden

Contractor: General Electric/RESR
Contract Number: F30602-73-C-0121
Effective Date of Contract: 16 April 1973
Contract Expiration Date: 31 July 1974
Amount of Contract: \$44,973.00
Program Code Number: 3E20
Period Covered: Feb 73 - Jul 74

Principal Investigator: Dr. P. Zavitsanos
Phone: 215 962-3496

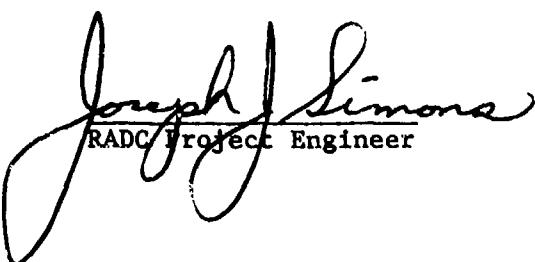
Project Engineer: Joseph J. Simons
Phone: 315 330-3055

Approved for public release;
distribution unlimited.

This research was supported by the Defense
Advanced Research Projects Agency of the
Department of Defense and was monitored by
Joseph J. Simons RADC (OCSE), GAFB NY 13441
under Contract F306020-73-C-0121, Job Order
No. 16490303.

This report has been reviewed by the RADC Information Office (OI),
and is releasable to the National Technical Information Service (NTIS).

This technical report has been reviewed and is approved.



Joseph J. Simons
RADC Project Engineer

TABLE OF CONTENTS

<u>SECTION</u>		<u>PAGE</u>
	ABSTRACT	1
I.	INTRODUCTION	2
II.	EXPERIMENTAL	2
	A. MATERIALS	2
	B. APPARATUS	2
	1. Induction Heating	2
	2. Laser Heating	3
III.	EXPERIMENTAL RESULTS	3
	1. Oxidation of Uranium by Molecular Oxygen	3
	2. The Oxidation of Thorium by Atomic Oxygen	7
	3. Oxidation of Thorium and Uranium by N_2O	10
IV.	CONCLUDING REMARKS	12
	REFERENCES	12

LIST OF FIGURES

<u>Figure No.</u>		<u>Page</u>
1	Knudsen Crucible Mass Spectrometer Apparatus.....	4
2	Laser Heating Experiment.....	5
3	Formation of Chemi-ions ThO^+ and ThO_2^+	9

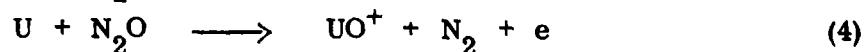
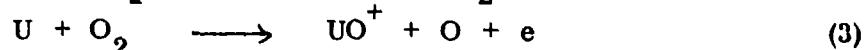
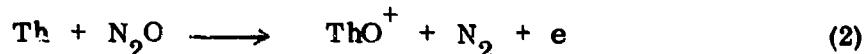
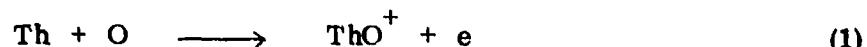
LIST OF TABLES

1	Rate Constant for the Formation of UO^+ from $\text{U} + \text{O}_2$	8
---	--	---

ABSTRACT

In an effort to understand the kinetics and mechanisms of gas-phase metal oxidation reactions, experiments were continued in an apparatus which utilizes RF heating and laser radiation for the production of the metal vapor and time-of-flight mass spectrometry for product identification and quantitative measurements of reactants and products.

Measurements were continued on the oxidation of thorium and uranium by molecular and atomic oxygen, as well as N_2O and rate constants were measured for following reactions:



where $k_1 = 3.1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$

$k_2 = 2.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$

$k_3 = 8.2 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$

$k_4 = 1.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$

I. INTRODUCTION

The oxidation of refractory metals in the gas phase is a relatively new area of research. Fite, et al¹ have recently published results on the oxidation of uranium vapor by molecular and atomic oxygen. The oxidation of gaseous thorium by molecular oxygen undertaken by Zavitsanos and Golden and some of the results were reported previously^{2,3}. Using experimental techniques developed and documented in previous reports³ the scope of the work was extended and rates were measured for other reactions involving thorium and uranium.

II. EXPERIMENTAL

A. MATERIALS

High purity samples of thorium "crystal bar" and uranium powder were obtained from Ventrol Metal Hydride Division, Beverly, Mass.

When Knudsen crucibles were used as containers, the structural material was tungsten. Best results, in terms of reducing background ThO and UO were obtained with single crystal tungsten liners.

B. APPARATUS

The heating methods considered for this study are induction RF heating and laser radiation.

1. Induction Heating

The use of RF heating in high-temperature mass spectrometric work has been previously demonstrated⁴ and utilized in obtaining temperatures as high as 3000°K.

The experimental arrangement is shown in Figure 1. Figure 1 shows the inductively heated Knudsen cell in-place in the Bendix Model 12 time-of-flight mass spectrometer. The water-cooled induction coil enters the furnace chamber from the bottom flange. The crucible and its holder are supported on three tantalum rods on the inlet assembly.

The Knudsen crucible dimensions are 0.25 in. I. D. x 0.45 in. deep with a 0.05 in. wall with a crucible cover, 0.125 in. thick x 0.35 in. dia., 60° conical orifice whose minor diameter is 0.03 in.

The temperature of the crucible is measured with a Leeds and Northrup manual optical pyrometer by sighting into the orifice (as shown in Figure 1). Corrections due to prism and window were made in all the reported temperature values.

The vapor generated in the crucible in Chamber II, after traveling 2 cm through a vacuum of $P_{II} 10^{-6}$ torr, enters Chamber I (through a slit 0.5 cm x .05 cm) and reacts with oxygen whose pressure P_I can be as high as 2×10^{-3} torr. The vapor travels 6 cm in Chamber I before it reaches point G where an electron beam of controlled energy is directed perpendicular to the metal vapor beam and its reaction products with oxygen. At this point, the ratio of unreacted metal oxide can be determined mass spectrometrically as a function of oxygen pressure and metal vapor density.

2. Laser Heating

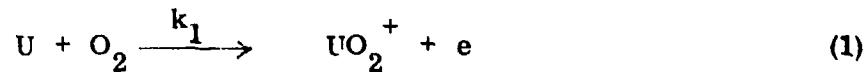
Another heating arrangement involves use of pulsed laser, ruby or CO_2 . The beam enters a chamber through a window (glass for ruby, $NaCl$ for CO_2) and strikes a metal target as shown in Figure 3. The generated vapor plume moves away from the metal surface and reacts with the surrounding oxygen. The ratio of metal vapor to oxidation products is measured with the time-of-flight mass spectrometer.

Special measurements on reactants and products are also made.

III. EXPERIMENTAL RESULTS

1. Oxidation of Uranium by Molecular Oxygen

A rate was reported by Fite for the reaction¹



When the oxygen pressure was increased 10^{-4} torr in addition to the above process another ion producing reaction was identified in the process of our work; that being

A - INDUCTION COIL
 B - TANTALUM HEAT SHIELD
 C - KNUDSEN CRUCIBLE AND LID
 D - WATER COOLED PORTION OF
 CHAMBER
 E - MOVABLE SHUTTER
 F - TOF SOURCE ENTRANCE SLIT

G - IONIZING ELECTRON BEAM
 H - ON GRID
 I - VIEWING WINDOW ON MULTIWINDOW
 ASSEMBLY
 J - PRISM
 K - OPTICAL PYROMETER

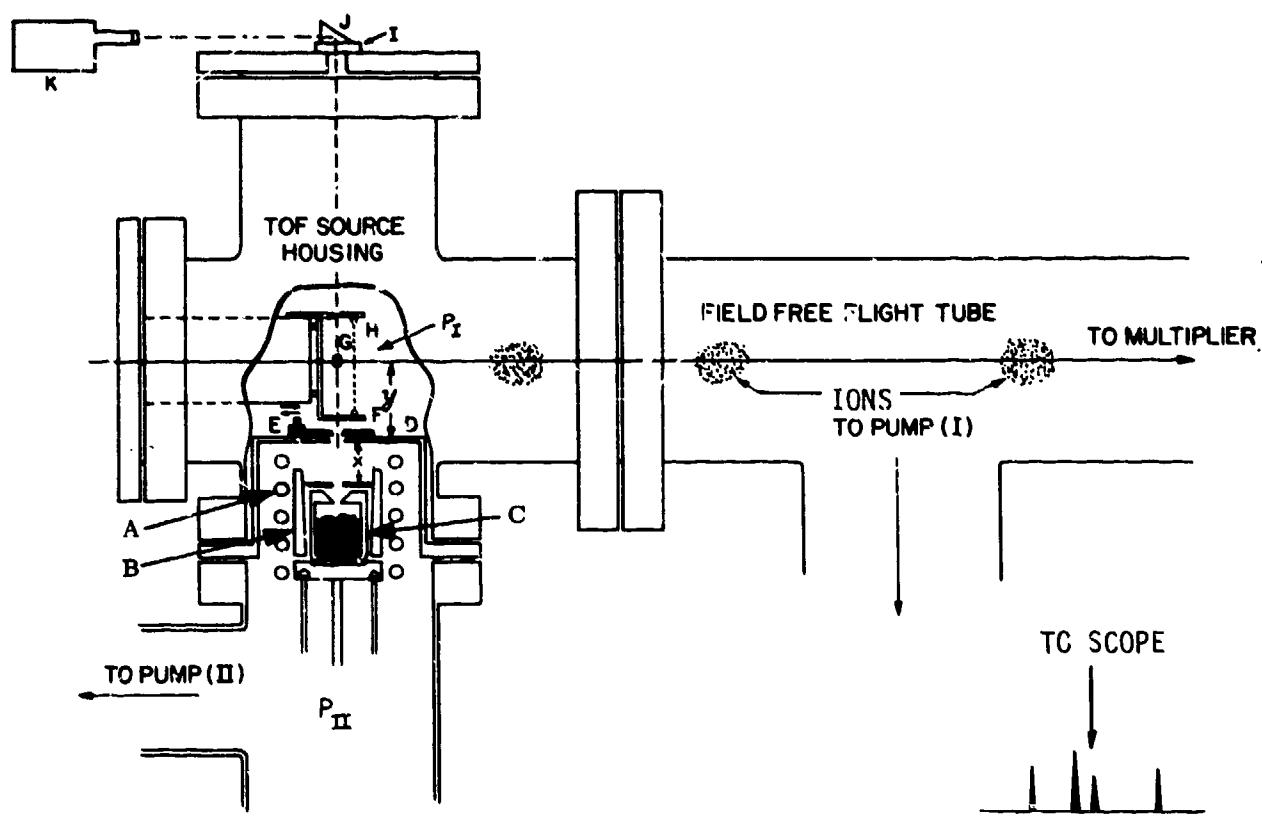


Figure 1 - KNUDSEN CRUCIBLE MASS SPECTROMETER APPARATUS

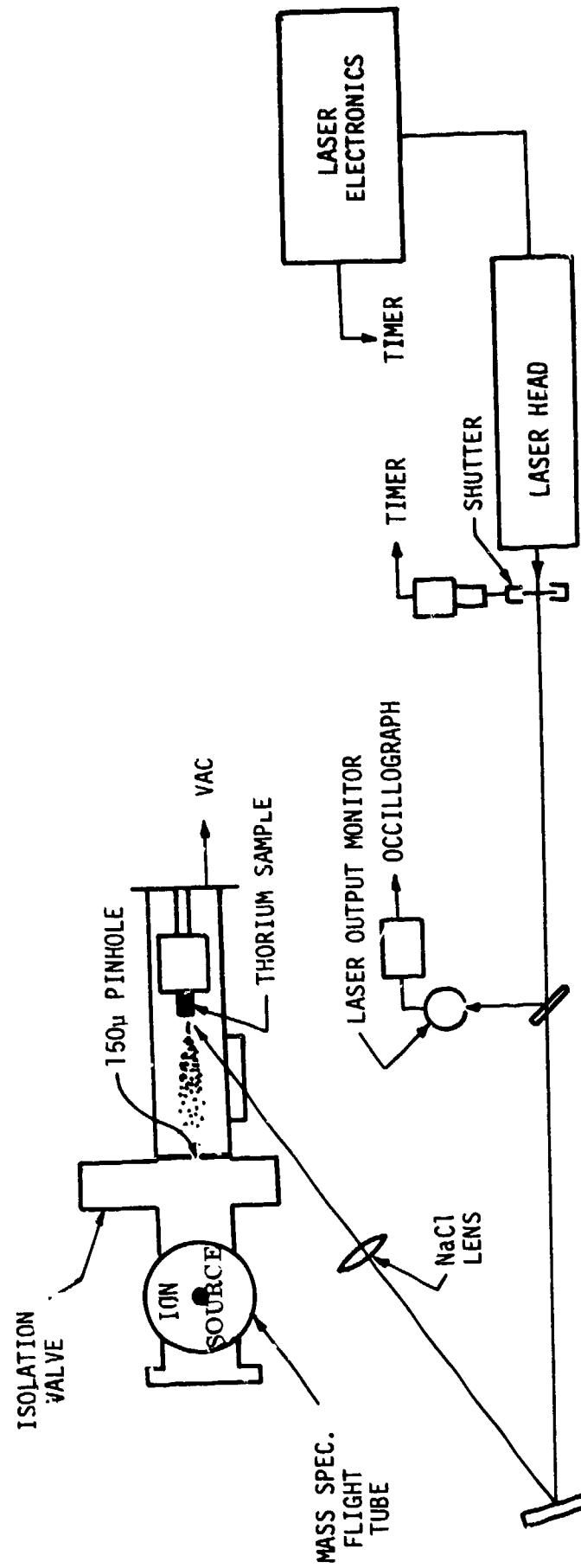
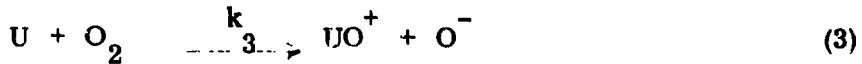
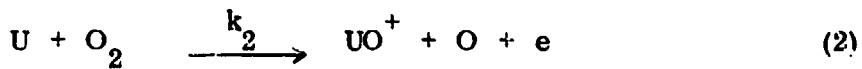


Figure 2 - LASER HEATING EXPERIMENT

the formation of UO_2^+ via one of the following two possible processes:



In order to identify the step accounting for the formation of UO_2^+ the polarity of the mass spectrometer was reversed in order to search for the negative ion O^- . In view of the fact that (under condition of equivalent sensitivity) no negative ion O^- was observed it was concluded that most the observed UO_2^+ was formed mainly via step (2). Unless of course the life of O^- is less than the flight time in the mass spectrometer which is of the order of 25 μsec . That is to say . at negative ions which loose their charge during flight time are not focussed properly and thus escape detection. The expressions describing ion formation in the U/O_2 system are :

$$\frac{d(\text{UO}_2^+)}{dt} = k_1 (\text{U}) (\text{O}_2) \quad \text{and}$$

$$\frac{d(\text{UO}_2^+)}{dt} = (k_2 + k_3) (\text{U}) (\text{O}_2) \approx k_2 (\text{U}) (\text{O}_2)$$

or
$$\frac{k_2}{k_1} = \frac{d(\text{UO}_2^+)}{d(\text{UO}_2^+)}$$

Since the product species UO_2^+ and UO_2^+ are expected to have nearly equal multiplier efficiencies it is expected that the ratio of ion intensities $I(\text{UO}_2^+)$, $I(\text{UO}_2^+)$ is equal to the ratio of rate constants k_2/k_1 under conditions of equal $(\text{U})/(\text{O}_2)$ ratios

$$\text{i.e. } \frac{k_2}{k_1} = \frac{I(\text{UO}_2^+)}{I(\text{UO}_2^+)}$$

$$\text{or } k_2 = k_1 \frac{I(\text{UO}_2^+)}{I(\text{UO}_2^+)}$$

It is therefore possible to determine k_2 (if k_1 is known) by measuring the intensity ratio of UO^+ and UO_2^+ formed simultaneously in the same run from reaction between U(g) and O_2 .

Several runs were made under conditions where the oxygen pressure was in the range $(1.1 - 4.4) \times 10^{-4}$ torr at two different temperatures 2273°K and 2323°K . (Under these conditions the number density of U(g) in the reaction chamber was several orders of magnitude lower than that of O_2). Data obtained from this series of experiments are shown in Table I along with the determination of $k_2 = (8.2 \pm 3) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$.

In view of the fact that reaction (2) is endothermic by 2 eV while reaction (3) is endothermic by only 0.5 eV a case can be made for the existence of O^- , in which case the value of k_2 represents the rate of UO^+ formation by reactions (2) or (3) or both. As far as it pertains to the intended application, however, it does not matter.

2. The Oxidation of Thorium by Atomic Oxygen.

The relative abundance of atomic oxygen in the upper atmosphere is high and reactions involving atomic oxygen are obviously important.

As part of this research several methods were examined in conjunction with atomic oxygen production; the method which proved successful in our case involved thermal decomposition of O_2 in an indium furnace, heated by the same induction field as the crucible containing the thorium.

When thorium was allowed to react with partially decomposed oxygen it became apparent that in addition to the formation of ThO_2^+ (which was reported before²) ThO^+ was observed as well, due to the following reactions

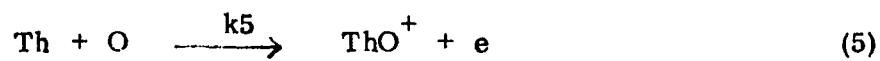
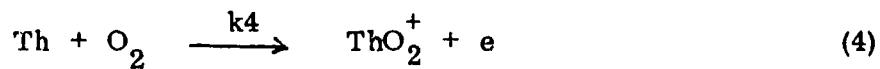


Figure 3 shows a typical mass spectrum of these two ions recorded in the absence of an ionizing electron beam. The intensity ratio of the observed ions

$$\frac{I(\text{ThO}^+)}{I(\text{ThO}_2^+)}$$

is related to the ratio of rate constants k_4 and k_5 and the degree of O_2 dissociation as follows:

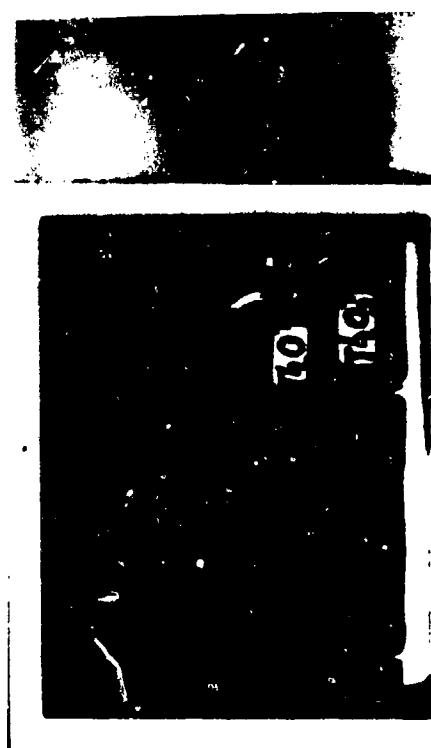
TABLE I

RATE CONSTANT FOR THE FORMATION OF UO^+ FROM $\text{U} + \text{O}_2$

CHILMI-ION INTENSITY I (UO^+)	I (UO^+)		$P_{\text{O}_2} \times 10^{-4}$ (torr)	$T^0 \text{K}$	k_2 ($\text{cm}^3 \text{molecule}^{-1} \text{sec}^{-1}$)
	I (UO_2^+)	I (UO_2^+)			
800	46,800	1.71×10^{-2}	4.4	2323	6.8×10^{-14}
600	23,000	2.61×10^{-2}	2.6	2323	10×10^{-14}
170	5,720	2.97×10^{-2}	1.1	2323	12×10^{-14}
200	30,055	1.02×10^{-2}	3.6	2273	4.1×10^{-14}

Average $(8.2 \pm 3) \times 10^{-14}$

FIGURE 3. FORMATION OF CHEMI-IONS ThC^+ AND ThO_2^+



$$\frac{I(\text{ThO}^+)}{I(\text{ThO}_2^+)} = \frac{k_5}{k_4} \times \frac{PO}{PO_2}$$

or $k_5 = k_4 \times \frac{I(\text{ThO}^+)}{I(\text{ThO}_2^+)} \times \frac{PO_2}{PO}$

Based on the equilibrium predictions at 2248°K at a total oxygen pressure of 10^{-3} torr the ratio of PO/PO_2 is 0.111. The observed ratio of chemi-ion intensities at the same temperature was:

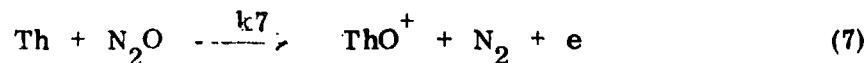
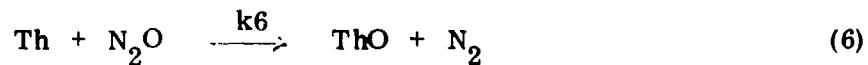
$$\frac{I(\text{ThO}^+)}{I(\text{ThO}_2^+)} = 7$$

therefore $k_5 = 63 \times k_4$

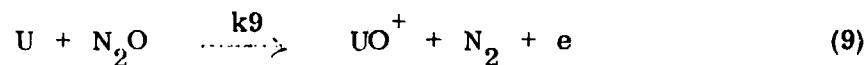
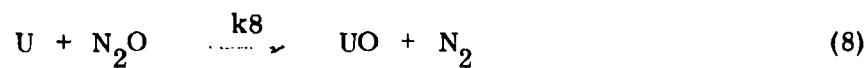
or* $= 63 \times 4.9 \times 10^{-12} = 3.1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$

3. Oxidation of Thorium and Uranium by N_2O

The first step in the oxidation of gaseous thorium and uranium by N_2O can proceed as follows:



and with uranium respectively



The formation of the neutral monoxides ThO and UO are highly exothermic by about 6 eV while the formation of UO^+ and ThO^+ are exothermic by 0.5 to 1 eV and are all thermodynamically favorable.

* k_4 was determined and reported in a previous report².

Data has been obtained thus far which allows determination of k_7 and k_9 via the ratio method (applied previously) which allows determination of one rate constant relative to another: In this case rates for reactions (7) and (9) were compared to corresponding rates of reactions (4) and (1). The corresponding relationships are:

$$k_7 = k_4 \times \frac{I(ThO_2^+)}{I(ThO_2^+)} \times \frac{P_{O_2}}{P_{N_2O}} \times \frac{I(Th^+)_{O_2}}{I(Th^+)_{N_2O}} \quad (10)$$

$$k_9 = k_1 \times \frac{I(UO_2^+)}{I(UO_2^+)} \times \frac{P_{O_2}}{P_{N_2O}} \times \frac{I(U^+)_{O_2}}{I(U^+)_{N_2O}} \quad (11)$$

The intensities of the metal ions were obtained with an ionizing electron beam set at 11 eV, and are proportional to the metal number density.

Two separate experiments were obviously required. One using O_2 as the oxidant the second N_2O .

$$I(Th^+)_{O_2}, I(U^+)_{O_2} \text{ and } I(Th^+)_{N_2O}$$

$I(U^+)_{N_2O}$ represent metal atom intensities as observed in the two

different experiments prior to the introduction of reactants O_2 and N_2O respectively. Thorium oxidation at 2273^0K under conditions where $P_{O_2} = 2.5 \times 10^{-4}$ torr, $P_{N_2O} = 4.2 \times 10^{-4}$ torr and $\frac{I(Th^+)_{O_2}}{I(Th^+)_{N_2O}} = 2.5$ resulted a ratio $\frac{I(ThO_2^+)}{I(ThO_2^+)} = 0.29$

and a value for

$$k_7 = 2.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$$

Similar treatment of uranium data resulted in a value of $k_9 = 1.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$

IV. CONCLUDING REMARKS

Based on results obtained to date the following conclusions can be made:

1. The oxidation of thorium in gas phase by molecular and atomic oxygen produces chemi-ions such as ThO_2^+ and ThO^+ respectively with corresponding rate constants $4.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ and $3.1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$.
The molecular oxygen reaction produces ThO at a (gas kinetic) rate of $(5.1 \pm 1.1) \times 10^{-10}$.
2. The oxidation of uranium by O_2 produces UO at gas kinetic rate, UO_2^+ with a rate constant $(4.9 \pm 2.4) \times 10^{-10}$ and UO^+ with rate constant 8.4×10^{-14} .
3. Reactions of both thorium and uranium with N_2O produce the monoxide ions ThO^+ and UO^+ with corresponding rate constants 2.2×10^{-12} and 1.2×10^{-12} .

REFERENCES:

1. W. L. Fite, H. H. Lo, and P. Irving, J. Chem. Phys. 60, 1236, (1974).
2. P. D. Zavitsanos, J. Chem. Phys. 59, 2162 (1973).
3. P. D. Zavitsanos and J. A. Golden, RADC-TR-73-376, Final Technical Report, October 1973, (AD 773 197)
4. P. D. Zavitsanos and G. Carlson, J. Chem. Phys. 59, 2966 (1973).

MISSION
of
Rome Air Development Center

RADC is the principal AFSC organization charged with planning and executing the USAF exploratory and advanced development programs for electromagnetic intelligence techniques, reliability and compatibility techniques for electronic systems, electromagnetic transmission and reception, ground based surveillance, ground communications, information displays and information processing. This Center provides technical or management assistance in support of studies, analyses, development planning activities, acquisition, test, evaluation, modification, and operation of aerospace systems and related equipment.

Source AFSCR 23-50, 11 May 70